Journal of Organometallic Chemistry 657 (2002) 194–204

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

X-ray analysis and structural characterization of 2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononenones

Hiram I. Beltrán, Luis S. Zamudio-Rivera, Teresa Mancilla, Rosa Santillan, Norberto Farfán *

Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, 07000 México, DF, Mexico

Received 15 October 2001; accepted 22 March 2002

Abstract

Nine new monomeric boronates of the type 2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-ones (**3a**–**3i**) were prepared from *N*-(2-hydroxybenzyl)-α-aminoacids **1a**–**1i** and phenylboronic acid **2** using 20:1 benzene–DMSO mixtures. The compounds were characterized by ^{1}H-, ^{13}C-, ^{11}B-, ^{15}N- and 2D-NMR (HETCOR, NOESY and COLOC) experiments, FT infrared, mass spectra and elemental analysis. Suitable monocrystals of *cis*-2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-one (**3a**), (2*S*,5*S*,6*R*)-2-phenyl-6-aza-1,3-dioxa-5-*sec*butyl-2-borabenzocyclononen-4-one (**3e**) and 2,5-diphenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-one (**3h**) were obtained and their structures are discussed. The X-ray structures, as well as the NMR data established that the configurations at the nitrogen and boron atoms are '*R*' and '*S*', respectively and the transannular fusion is *cis*. A semi-empirical (SAM1) study allowed calculation of the energy for all possible stereoisomers, showing that the stabilization increases as the THC (TetraHedral Character of the boron atom) increases and also as the N→B bond distance decreases, in agreement with the experimental results. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Boron compounds; X-ray structures; NMR; Boronates

1. Introduction

N-(2-Hydroxy)benzyl-α-aminoacids have been used as chelating agents with triethoxyborane [1] and some transition metal compounds, like copper [2–4], zinc [2], cobalt [2], nickel [2] and manganese [5]. They have also been used as carriers of technetium radioisotopes for kinetic biodistribution studies *in vivo* [6].

As part of our research on boron macrocycles we have described the synthesis of a series of monomeric, dimeric, trimeric and tetrameric boronates derived from tridentate ligands [7–12], which possess one nitrogen and two oxygen donor atoms (Scheme 1). The results have shown that in all cases the nitrogen atom is coordinated to boron [12] propitiating the assembly of the macrocycles, while the oxygens are involved in the formation of five- or six-membered rings and intermolecular boron–oxygen bonds. Moreover, the reaction is dependent on steric, as well as electronic factors. In the reaction of 2,6-pyridinedimethanol and phenyl boronic acid, a boronate tetrameric structure containing four 5-membered and one 20-membered rings, was obtained through a self-assembled process [7]. All these compounds showed high hydrolytic stability due to the tetracoordination of the boron atoms.

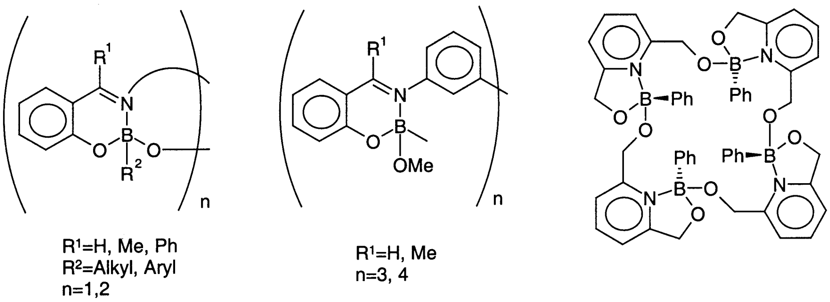
In previous reports, it has been described that the formation of dimeric and monomeric structures is highly dependent on reaction conditions as well as the structure of the salicylidenimino alcohols, thus it is possible in certain cases to obtain either the dimeric or monomeric derivatives in high yields by using kinetic or thermodynamic control (Scheme 2) [13]. In all cases, the boron atom shows a distorted tetrahedral geometry and the N→B bonds are between 1.6 and 1.7 Å, which are characteristic for dative nitrogen boron bonds [7–13].

---

* Corresponding author. Tel.: +52-5557-473721; fax: +52-5557-477113.

E-mail address: jfarfan@mail.cinvestav.mx (N. Farfán).

PII: S0022-328X(02)01418-3



Scheme 1. Monomeric, dimeric, trimeric and tetrameric boronates.

Concerning the stereochemistry at the transannular fused rings involving the N → B bond, a literature search shows that the *cis* stereoisomer is formed in preference to the *trans* [14–35].

Herein, we describe the preparation and complete characterization of nine new boronates of the type 2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-ones (**3a**–**3i**) prepared from *N*-(2-hydroxybenzyl)-α-aminoacids **1a**–**1i** and phenylboronic acid **2** using a 20:1 mixture of benzene–DMSO. The compounds were characterized by ^{1}H-, ^{13}C-, ^{11}B-, ^{15}N- and 2D-NMR (HETCOR, NOESY and COLOC) experiments, FT infrared, mass spectra and elemental analysis. Suitable monocrystals of *cis*-2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-one (**3a**), (2*S*, 5*S*, 6*R*)-2-phenyl-6-aza-1,3-dioxa-5-*sec*-butyl-2-borabenzocyclononen-4-one (**3e**) and 2,5-diphenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-one (**3h**) were obtained and discussed.

2. Results and discussion

2.1. Synthesis of 2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-ones 3a–3i

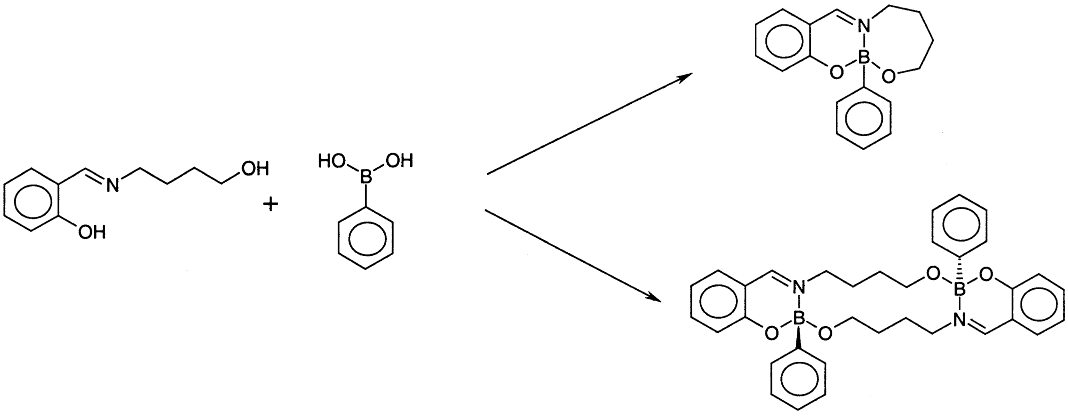
The condensation reaction of known tridentate ligands **1a**–**1i** [36] and phenylboronic acid **2** was carried out as described in the literature [15,16] to obtain 2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-ones **3a**–**3i** in 68–97% yields (Scheme 3). These tricyclic derivatives show transannular N → B fusion, 5- and 6-membered rings and a tetrahedral geometry for the boron and nitrogen atoms [37].

2.2. Spectroscopic information

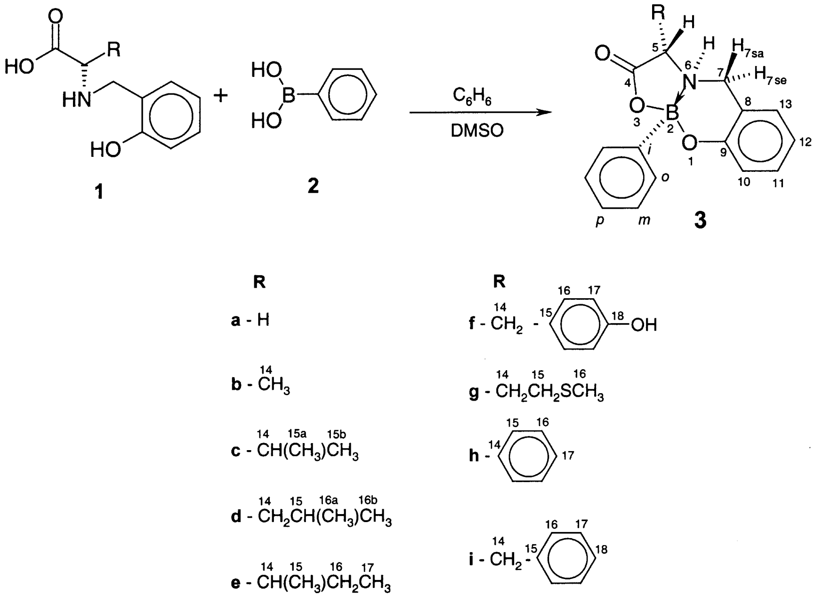
The ^{1}H and ^{13}C chemical shift assignments for **3a**–**3i** are listed in Tables 1 and 2, respectively. The assignments are based on 2D HETCOR, NOESY and COLOC NMR data.

The ^{1}H-NMR spectra of **3a**–**3i** showed characteristic couplings of 7.4–1.0 Hz between H-5 and H-6, and 2.9–1.5 Hz between H-6 and H-7 *se* (*se* = pseudoequatorial). All compounds show an AB system in the ^{1}H-NMR spectra for the methylene at position 7, except for the glycine derivative **3a**. The chemical shift difference for the AB system in **3b**–**3i** is larger compared with the corresponding ligands ($\Delta\delta = 15.8$ Hz) [36]. Moreover, the $\Delta\delta$ for benzyl substituted derivatives (**3f** and **3i**) is in the range of 240.0 Hz compared with the remaining derivatives which show a difference of 74.3 Hz.

The ^{13}C-NMR spectra show the carbonyl signal (C-4) in the expected range for boronate esters (174.1–171.3 ppm), the C-5 shift is in the range of 56.3–66.6 ppm except for compound **3a** (50.0 ppm). The carbon in position 7 appears in the range between 45.8 and 49.4



Scheme 2. Formation of monomeric and dimeric structures.



Scheme 3. Synthesis of boronates **3a**–**3i**.

ppm. The *ipso* carbon attached to boron shows chemical shifts from 141.8 to 143.2 ppm and is observed as a broad signal (Table 2).

Formation of the tricyclic structure was evidenced by the ^{11}B chemical shift which appears in the range from +6.04 to +4.94 ppm, characteristic for tetracoordinated boronate esters [38] and by the ^{15}N-NMR signals, in the range from −335.1 to −318.5 ppm, demonstrating that the nitrogen atoms are tetracoordinated [39].

The relative configuration at the H–N→B–Ph fragment was determined through NOESY experiments and confirmed by the X-ray analyses of compounds **3a**, **3e** and **3h**. The absolute configuration established by these methods is '*R*' for nitrogen and '*S*' for boron except for **3a** and **3h**, which underwent partial racemization under the reaction conditions, as confirmed by ^{1}H and ^{13}C-NMR experiments using chiral shift reagents.

The IR spectra of compounds **3a**–**3i** show the carbonyl band in the range 1740–1710 cm^{-1}. In all cases, the mass spectra showed the molecular ion and the loss of phenyl and benzene groups from the M^{+} to give tricyclic structures with covalent bonds between the boron and nitrogen atoms.

2.3. *Molecular structures of* ***3a****,* ***3e*** *and* ***3h***

Crystallographic data for **3a**, **3e** and **3h** are listed in Table 3, selected bond lengths, angles, torsion angles and plane deviations are summarized in Table 4, and molecular structures are shown in Figs. 1 and 2. Compounds **3e** and **3h** crystallized with two independent molecules in the asymmetric unit. The fact that compound **3h** crystallized in a centrosymmetric space group indicated that racemization had occurred. The N→B distances found are as follows: 1.667 Å for **3a**, 1.659 and 1.612 Å for **3e**, 1.627 and 1.635 Å for **3h**, in agreement with the distances found in similar derivatives described in the literature [14–36], the B–O$_{\text{carboxylate}}$ distances present the following values: 1.497 Å for **3a**, 1.507 and 1.511 Å for **3e**, 1.514 and 1.498 Å for **3h** and they shown a resonance stabilization due to the carboxylic fragment [40,41], the B–O$_{\text{phenolic}}$ distances have values of 1.436 Å for **3a**, 1.429 and 1.420 Å for **3e**, 1.432 and 1.425 Å for **3h** in agreement with the literature values for the same fragment [1]. The structures possess similar dihedral angles for the H–N→B–Ph fragment, the differences are due to the nature of the R substituent in position 2, resulting in dihedral angles of −0.73° for **3a**, 3.80 and 9.41 for **3e** and finally 31.84° and 32.23° for **3h**. Also there exist intermolecular hydrogen bonds between the NH proton and the carbonyl oxygen (O2) of the COOB fragment with magnitudes of 1.961 Å for **3a**, 1.930 and 2.030 Å for **3e**, 2.068 and 2.131 Å for **3h** (Figs. 3 and 4). In all cases, the 6-membered ring containing the B–N–C(3)–C(4)–C(5)–O(3) fragment has a boat conformation, and the 5-membered ring formed by the B–N–C(2)–C(1)–O(1) moiety in **3a** is nearly planar, **3e** is a half-chair with the boron and carbonyl carbon atoms out of plane and **3h** shows an envelope conformation, with the nitrogen atom lifted out of the plane due to the presence of a phenyl group directly attached to C(2).

The tetrahedral character (THC) of the boron atom [42] was a useful parameter to evaluate the geometry of the boron atom for those compounds that crystallized (**3a**, **3e** and **3h**). The magnitudes are %THC = 78.52 for **3a**, 77.54 and 79.31 for **3e**, %THC = 72.32 and 74.80 for **3h**. It is important to mention that the lowest bond angle measured corresponds to the O(1)–B–N angle with

Table 1
^{1}H-NMR data of compounds **3a**–**3i** δ (ppm) in DMSO-d_6

Compound	H-5	H-6	H-7se	H-7sa	H-10	H-11	H-12	H-13	B-C_6H_5		
									ortho	*meta*	*para*
3a	3.93 d, $J = 14.1$ 2H	8.40 s 1H	4.17 d, $J_{AB} = 13.9$ 1H	3.42 $J_{AB} = 13.9$ 1H	6.94 d, $J_o = 7.8$ 1H	7.30 t, $J_o = 7.8$ 1H	6.93 t, $J_o = 8.6$ 1H	7.34 m 1H	7.56–7.51 m 2H	7.38–7.31 m 2H	7.31 t, $J_o = 7.4$ 1H
3b	3.55 q, $J = 7.1$ 1H	8.00 bd, $J = 7.0$ 1H	4.14 dd, $J_{AB} = 14.8$ $J_{NH} = 2.4$, 2H	4.04 $J_{AB} = 14.8$ 1H	6.89 d, $J_o = 8.0$ 1H	7.30 t, $J_o = 8.0$ 1H	6.89 t, $J_o = 7.7$ 1H	7.26 d, $J_o = 7.7$ 1H	7.50–7.47 m 2H	7.33–7.30 m 2H	7.33–7.30 m 1H
3c	3.42 dd, $J = 5.7$ $J = 3.1$, 1H	7.55 sb 1H	4.23 dd, $J_{AB} = 13.9$ $J_{NH} = 1.8$, 1H	3.92 $J_{AB} = 13.9$ 1H	6.90 d, $J_o = 8.1$ 1H	7.39–7.30 m 1H	6.94 t, $J_o = 7.3$ 1H	7.39–7.30 m 1H	7.56–7.50 m 2H	7.39–7.30 m 2H	7.39–7.30 m 1H
3d	3.36 c, $J = 6.8$ 1H	8.03 bd, $J = 6.8$ 1H	4.21 dd, $J_{AB} = 14.4$ $J_{NH} = 2.4$, 1H	3.93 $J_{AB} = 14.4$ 1H	6.92 d, $J_o = 7.3$ 1H	7.34–7.32 m 1H	6.93 t, $J_o = 7.4$ 1H	7.28 d, $J_o = 7.4$ 1H	7.53–7.50 m 2H	7.34–7.32 m 2H	7.34–7.32 m 1H
3e	3.40 dd, $J = 2.8$ $J_{NH} = 1.0$,1H	7.56–7.54 m 1H	4.20 bd, $J_{AB} = 13.7$ 1H	3.94 $J_{AB} = 13.7$ 1H	6.89 d, $J_o = 8.1$ 1H	7.34–7.27 m 1H	6.93 t, $J_o = 7.3$ 1H	7.34–7.27 m 1H	7.56–7.54 m 2H	7.34–7.27 m 2H	7.34–7.27 m 1H
3f	3.71 ddd, $J = 8.7$,6.9, 4.2 1H	7.95 bd, $J_{NH} = 6.9$ 1H	4.18 bd, $J_{AB} = 14.2$ 1H	3.36 $J_{AB} = 14.2$ 1H	6.87 d, $J_o = 7.8$ 1H	7.29–7.22 m 1H	6.85 t, $J_o = 7.0$ 1H	6.81 d, $J_o = 7.0$ 1H	7.38–7.36 m 2H	7.29–7.22 m 2H	7.25–7.22 m 1H
3g	3.64 c, $J = 6.5$ 1H	8.02 bd, $J_{NH} = 2.9$ 1H	4.18 dd, $J_{AB} = 14.3$ $J_{NH} = 2.9$,1H	3.96 d, $J_{AB} = 14.3$ 1H	6.91 d, $J_o = 7.7$ 1H	7.28 t, $J_o = 7.7$ 1H	6.92 t, $J_o = 7.7$ 1H	7.26 d, $J_o = 7.7$ 1H	7.53–7.51 m 2H	7.35–7.32 m 2H	7.35–7.32 m 1H
3h	4.69 d, $J_{NH} = 6.7$ 1H	8.33 bd, $J_{NH} = 6.7$ 1H	4.18 dd, $J_{AB} = 14.3$ $\mathrm{J}_{NH} = 1.5$,1H	4.01 $J_{AB} = 14.3$ 1H	6.96 d, $J_o = 8.3$ 1H	7.29–7.22 m 1H	6.98 t, $J_o = 7.8$ 1H	7.31–7.29 m 1H	7.62–7.57 m 2H	7.35–7.32 m 2H	7.38–7.36 m 1H
3i	3.82 ddd, $J = 8.7$, 4.7 $J_{NH} = 7.4$, 1H	8.14 bd, $J_{NH} = 7.4$ 1H	4.08 dd, $J_{AB} = 13.2$ $\mathrm{J}_{NH} = 1.8$, 1H	3.33 $J_{AB} = 13.2$ 1H	6.88 d, $J_o = 7.7$ 1H	7.34–7.32 m 1H	6.85 t, $J_o = 7.4$ 1H	6.79 d, $J_o = 6.6$ 1H	7.43–7.40 m 2H	7.30–7.29 m 2H	7.25–7.22 t, $J_o = 7.9$ 1H

3b: H-14, 1.40, d, $J = 7.3$, 3H. **3c**: H-14, 2.26, dhp, $J = 7.0$, 5.7, 1H; H-15, 1.01, d, J = 7.0, 6H. **3d**: H-14, 1.70, t, $J = 7.1$, 2H; H-15, 1.96, hp, $J = 6.8$, 1H; H-16a, 0.89, d, $J = 6.8$, 3H; H-16b, 0.86, d, $J = 6.8$, 3H. **3e**: H-14, 1.94, dd, $J = 12.3$, 8.2, 1H; H-15, 0.84, t, $J = 6.4$, 3H; H-16a, 1.52–1.44, m, $J = 6.6$, 1H; H-16b, 1.42–1.33, $J = 6.4$, m, 1H; H-17, 0.95, d, $J = 6.2$, 3H. **3f**: H-14a, 3.16, dd, $J_{AB} = 14.5$, $J_{AX} = 4.2$, 1H; H-14b, 3.00, dd, $J_{AB} = 14.5$, $J_{BX} = 8.7$, 1H; H-16, 7.13, d, $J_o = 8.2$, 2H; H-17, 6.77, d, $J_o = 8.2$, 2H; H–OH, 9.40, bs, 1H. **3g**: H-14, 2.76–2.64, m, 2H; H-15, 2.17–2.01, m, 2H; H-16, 2.03, s, 3H. **3h**: H-15, 7.39–7.37, m, 2H; H-16, 7.46–7.44, m, 2H; H-17, 7.46–7.44, 1H. **3i**: H-14a, 3.29, dd, $J_{AB} = 14.6$, $J_{AX} = 8.7$; H-14b, 3.13, dd, $J_{AB} = 14.6$, $J_{BX} = 4.7$, 1H; H-16, 7.34–7.32, m, 2H; H-17, 7.34–7.32, m, 2H; H-18, 7.30–7.29, m, 2H. se, pseudoequatorial; sa, pseudoaxial; s, singlet; bs, broad singlet; d, doublet; bd, broad doublet; t, triplet; c, quadruplet; q, quintuplet; ddt, double double of triplet; hp, heptet; dhp, double of heptets; m, multiplet.

Table 2
^{13}C, ^{15}N and ^{11}B-NMR data of compounds **3a**–**3i**. δ (ppm) in DMSO-d_6

Compound	C-4	C-5	C-7	C-8	C-9	C-10	C-11	C-12	C-13	B-C_6H_5				^{15}N	^{11}B
										ipso	*ortho*	*meta*	*para*		
3a	171.3	50.0	47.9	120.5	156.2	119.1	129.6	120.7	130.6	142.7	132.3	127.9	128.3	−335.1	+5.66
3b	174.1	56.3	45.8	118.9	155.9	118.7	129.5	120.3	130.3	142.8	132.3	127.8	128.2	−324.5	+4.95
3c	172.8	66.6	49.4	119.4	156.7	121.2	130.3	121.7	131.0	142.8	133.0	128.1	128.6	−326.5	+5.15
3d	174.1	58.5	47.7	119.2	156.6	120.3	131.0	121.0	132.8	143.2	132.8	128.2	128.6	−324.0	+4.94
3e	172.3	65.1	48.5	121.1	156.4	119.1	129.9	120.9	130.7	142.7	132.6	127.8	128.3	−325.9	+5.07
3f	172.4	60.3	46.1	118.0	155.6	118.1	127.8	119.8	128.9	142.3	132.1	127.2	129.9	−325.8	+5.08
3g	173.3	58.9	47.4	120.0	156.1	118.9	129.6	120.6	130.6	142.6	132.4	127.9	128.3	−325.1	+6.04
3h	171.7	64.4	46.7	119.1	155.7	118.5	127.8	120.3	130.1	142.5	132.0	127.4	129.5	−318.5	+5.01
3i	172.3	60.0	46.0	117.8	155.5	118.1	127.8	119.8	128.9	141.8	131.8	127.3	130.0	−325.7	+5.06

3b: C-14, 14.4. **3c**: C-14, 29.6; C-15a, 18.3; C-15b, 18.7. **3d**: C-14, 39.8; C-15, 25.0; C-16a, 22.4; C-16b, 23.1. **3e**: C-14, 35.6; C-15, 25.6; C-16, 12.3; C-17, 14.9. **3f**: C-14, 33.7; C-15, 126.3; C-16, 130.4; C-17, 115.3; C-18, 156.5. **3g**: C-14, 29.7; C-15, 29.6; C-16, 14.6. **3h**: C-14, 132.9; C-15, 129.6; C-16, 128.9; C-17, 129.3. **3i**: C-14, 34.5; C-15, 136.6; C-16, 128.5; C-17, 129.3; C-18, 127.1.

Table 3
X-ray data for **3a**, **3e** and **3h**

Compound	**3a**	**3e**	**3h**
Chemical formula	$C_{15}H_{14}BNO_3$	$C_{19}H_{22}BNO_3$	$C_{21}H_{18}BNO_3$
Molecular weight	267.08	323.19	343.18
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
Cell parameters			
a (Å)	7.563(4)	12.803(4)	11.773(5)
b (Å)	9.580(2)	12.810(4)	16.430(9)
c (Å)	18.798(2)	22.071(6)	18.764(3)
α (°)	90	90	90
β (°)	98.66(3)	90	92.16(3)
δ (°)	90	90	90
V (Å^3)	1346.4(8)	3619.8(19)	3627.0(30)
Z	4	8	8
$\rho_{(calc)}$ (Mg m^{-3})	1.318	1.186	1.257
μ (mm^{-1})	0.091	0.079	0.083
Collected reflections	2941	6824	5169
$R_{(int.)}$	0.0141	0.0000	0.0464
Data	2732	3417	4892
Parameters	237	499	517
Goodness-of-fit on F^2	1.020	1.041	0.964
R	0.0388	0.0545	0.0544
R_w	0.0903	0.1447	0.1053

values of 99.60° for **3a**, 98.93 and 99.80° for **3e**, 97.58 and 98.83° for **3h**, this can be attributed to ring fusion and strain in the 5-membered ring.

2.4. Semi-empirical calculations of boronates 3–6

In order to evaluate the influence of steric factors on this reaction, the geometry for all possible stereoisomers was determined using a theoretical (AM1) approach.

The computational study was performed with the Hyperchem program [43] for semi-empirical calculations (AM1 method). A full set of semi-empirical optimizations was carried out to determine the main preferences to obtain just the 2(*S*), N(*R*), B(*S*) products (**3a**–**3i**), all the stationary points were classified as minima by Hessian matrix calculations with the same method (AM1). The coordinates for SAM1 calculations were obtained from X-ray data.

In compounds **3b**–**3i** the presence of two new stereogenic centers (nitrogen and boron) leads to four possible diastereoisomers with fixed configuration at C-5, while the glycine derivative **3a** does not possess a stereogenic center and therefore gives only two diastereoisomers (Fig. 5).

Table 5 summarizes selected information obtained with the semi-empirical calculations for all the stereoisomers (**3**–**6**). The calculated properties for each stereoisomeric serie (**3**, **4**, **5** and **6**, respectively) show that the THC character increases as the energy decreases, thus **3** > **4** > **5** > **6**. Also the bond length is inversely proportional to the THC thus the N→B bond length increases in the serie **3** > **4** > **5** > **6**, while the energy increases as the bond length increases (**3** > **4** > **5** > **6**).

The results show that there is an important steric effect controlling the formation of this fused compounds, the averaged difference in energy between the *cis* and *trans* fused derivatives is −14.53 kcal mol^{-1}. However, in the case of related pairs such as **3**–**5** and **4**–**6**, the difference is smaller, in the range of −1.5 to −8.0 kcal mol^{-1} depending on the substituent. For compounds **3** and **4** there are two eclipsed interactions while **5** and **6** show four *gauche* interactions. The deformation of the fused structure (*cis* or *trans*) depends directly on the substituent effect as evidenced by the H–N–B–Ph torsion angles.

Table 4
Selected bond distances (Å), bond angles (°), torsion angles (°), plane deviations (Å) and THC (%) for **3a**, **3e** and **3h**

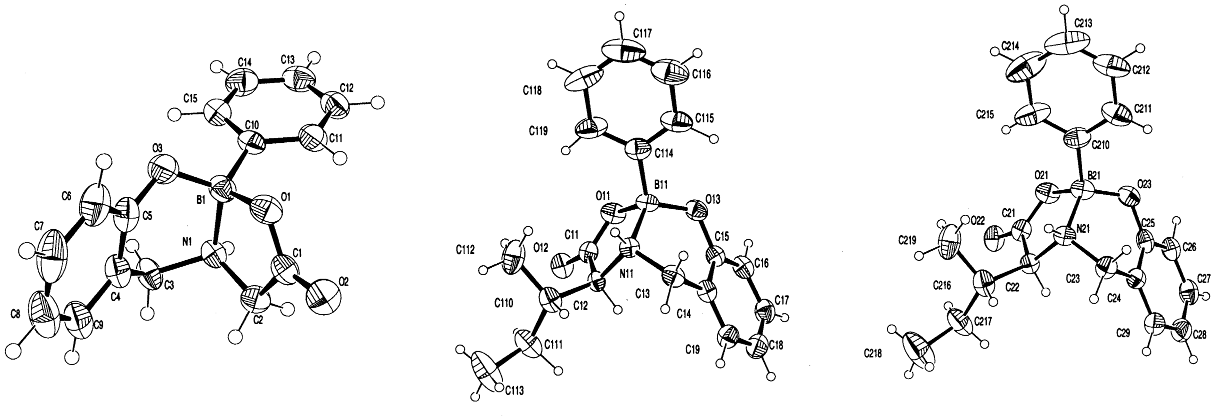
	3a	**3b**		**3c**	
		Mol. 1	Mol. 2	Mol. 1	Mol. 2
Bond distances (Å)					
B–N	1.667(3)	1.659(12)	1.612(12)	1.627(7)	1.635(7)
B–O(3)	1.436(2)	1.429(12)	1.420(12)	1.432(7)	1.425(6)
B–O(1)	1.497(2)	1.507(11)	1.511(11)	1.514(7)	1.498(6)
B–C(10)	1.587(3)	1.592(14)	1.606(14)	1.553(8)	1.580(7)
C(1)–O(1)	1.314(2)	1.291(10)	1.299(9)	1.301(6)	1.301(6)
C(1)–O(2)	1.203(2)	1.222(9)	1.225(9)	1.206(6)	1.207(5)
C(1)–C(2)	1.507(3)	1.513(11)	1.510(11)	1.517(7)	1.517(6)
C(2)–N	1.481(2)	1.507(10)	1.504(10)	1.481(6)	1.506(6)
N–C(3)	1.501(2)	1.499(11)	1.482(10)	1.478(5)	1.491(6)
N–H	0.954(20)	0.904(84)	0.884(79)	0.974(62)	0.842(37)
Bond angles (°)					
O(1)–B–N	99.60(14)	98.93(64)	99.80(66)	97.58(44)	98.83(40)
O(3)–B–N	109.84(15)	109.78(71)	111.31(75)	110.02(48)	108.36(43)
O(1)–B–O(3)	109.78(15)	112.08(75)	109.71(75)	108.17(54)	109.36(44)
O(1)–B–C(10)	113.51(15)	110.49(76)	110.14(74)	112.91(55)	111.87(44)
N–B–C(10)	109.17(15)	112.11(74)	113.71(78)	111.48(52)	114.37(44)
O(3)–B–C(10)	113.97(16)	112.68(72)	111.55(83)	115.25(59)	113.09(46)
H–N–B	109.35(119)	106.75(544)	108.15(521)	105.54(367)	107.93(260)
B–N–C(2)	106.01(14)	107.02(61)	107.56(62)	104.90(44)	103.76(39)
B–N–C(3)	112.02(15)	112.15(67)	113.07(66)	112.24(44)	115.04(42)
C(2)–N–C(3)	114.28(14)	111.34(63)	112.38(62)	116.40(44)	114.87(42)
H–N–C(2)	105.99(110)	115.49(532)	109.60(517)	107.78(344)	109.20(258)
H–N–C(3)	108.94(112)	104.11(534)	105.99(517)	109.33(351)	105.84(254)
Torsion angles (°)					
H–N–B–C(10)	−0.73	3.80	9.41	31.84	32.23
O(1)–B–N–C(2)	−6.02	11.49	10.47	27.23	29.06
O(3)–B–N–C(3)	4.04	16.42	19.37	41.98	41.49
Plane Deviation (Å)					
Plane 1					
C(3)–C(4)–C(5)–C(6)–C(7)–C(8)–C(9)–O(3)					
N	1.0188	0.9713	−0.9499	0.5761	−0.5657
B	0.9510	0.7406	−0.7192	0.0912	−0.0722
Plane 2					
O(1)–C(1)–C(2)–O(2)					
N	0.1038	−0.1473	−0.1360	0.5142	0.4898
B	−0.0035	0.0539	0.0515	0.0508	−0.0150
%THC of B	78.52	77.54	79.31	72.32	74.80

3. Conclusions

In conclusion, boron compounds derived from tridentate ligands **1a**–**1i** yield five- and six-fused membered rings due to N → B bond formation (**3a**–**3i**). In all cases, the ring fusion for the H–N → B–Ph fragment is *cis* and the reaction is highly stereoselective yielding structures with '*S*' configuration for the boron atom and '*R*' for the nitrogen (for compounds **3b**–**3g**, and **3i**), this was demonstrated by 2D-NMR NOESY experiments and confirmed by the X-ray analysis of compounds **3a**, **3e** and **3h**. While there is an increased tension in the five-membered ring, hence the deformation of the boron atom from the idealized tetrahedron geometry is in an average of 76.5%. The theoretical calculations are in good agreement with the experimental data and the THC is a powerful tool to evaluate the stabilization of such molecules. The results show that the greater the stabilization of the compounds, the greater the THC value, also there is a significant influence of the configuration of these newly formed stereogenic centers on the N → B bond lengths. Compounds **3a**–**3i** are stable in aprotic solvents and biological evaluation is under progress.

4. Experimental

NMR experiments were performed on a JEOL Eclipse+400 spectrometer at room temperature (r.t.).



Compound **3a**.

Compound **3e**.

Fig. 1. Perspective view of the molecular structure of compounds **3a** and **3e**.

All ^{1}H and ^{13}C resonances are reported relative to TMS, ^{15}N resonances are relative to neat $MeNO_2$, ^{11}B spectra was obtained relative to $BF_3 \cdot OEt_2$ and all the samples were determined using DMSO-d_6 as solvent. The IR spectra were recorded as KBr pellets on a Perkin–Elmer 16F PC FT-IR spectrometer. Mass spectra were obtained on a Hewlett-Packard 59940-A spectrometer at 20 eV electron impact. Melting points were measured in open capillary tubes on a Gallenkamp MFB 595 apparatus and have not been corrected. Elemental analyses were determined in a Barioel equipment. X-ray diffraction analyses were determined on an Enraf Nonius-CAD4 diffractometer.

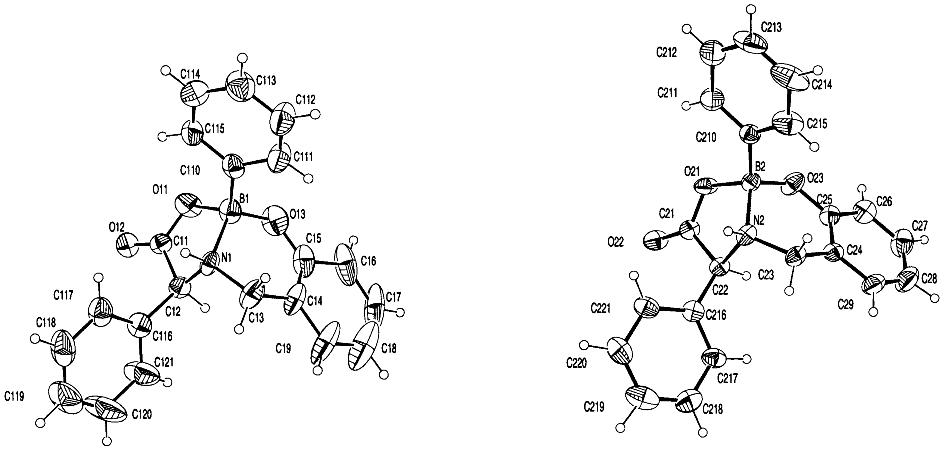
4.1. General procedure. Preparation of 2-phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-ones (3a–3i)

A 0.5 g (2.76 mmol) quantity of compound **1a** was added to a flask which contained 0.337 g (2.76 mmol) of phenylboronic acid **2**, 80 ml of C_6H_6 and 1–3 ml of DMSO were added and the solution was refluxed for 8 h. The solvent was removed under vacuum and the residue dissolved in methylene chloride and CH_3COCH_3. The product was precipitated by addition of C_6H_{14}, obtaining 0.597 g (2.236 mmol, 81%) of compound **3a**.

The remaining compounds (**3b**–**3i**) were prepared using the molar ratios reported in the general procedure.

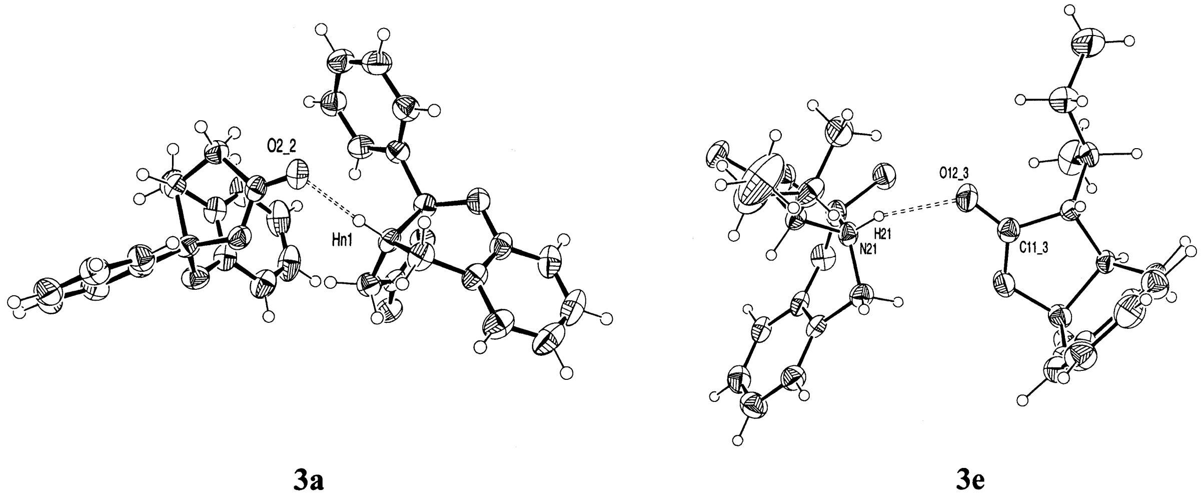
4.1.1. 2-Phenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-one (3a)

Compound **3a**. White solid, 81.0% yield, m.p. 203–205 °C. IR (ν) (KBr); 3118 (NH), 3072, 3046, 2908, 1740 (COOB), 1728 (COOB), 1608, δ 1506 (NH), 1488, 1460, 1320, 1294, 1268, 1250, 1240, 1220, 1060, 1030, 1014, 974, 770, 748, 704, 698 cm^{-1}; MS *m/z* (%): 268 ($M^{+}+1$, 4), 267 (M^{+}, 16), 208 (11), 190 (28), 189 (91), 188 (85), 187 (16), 162 (100), 161 (27), 107 (16), 78 (15).



Compound **3h**.

Fig. 2. Perspective view of the molecular structure of compound **3h**.



3a **3e**

Fig. 3. Perspective view of the intermolecular interaction of compounds **3a** and **3e**.

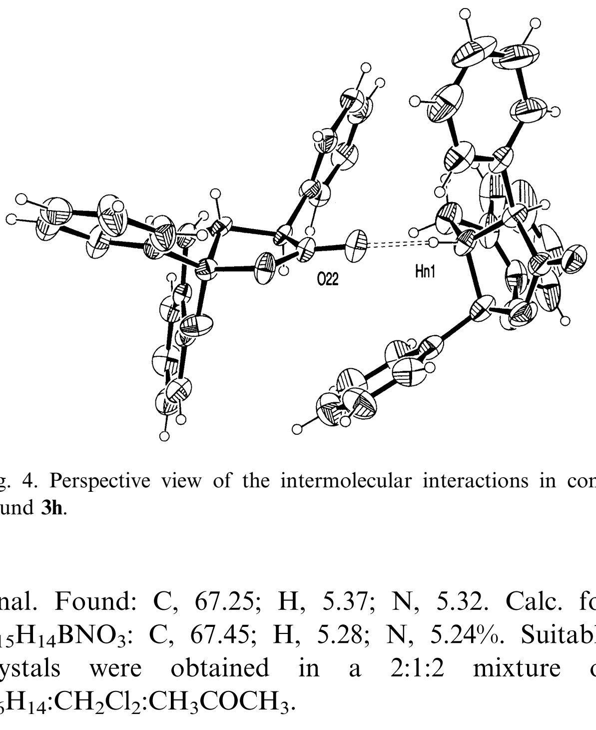


Fig. 4. Perspective view of the intermolecular interactions in compound **3h**.

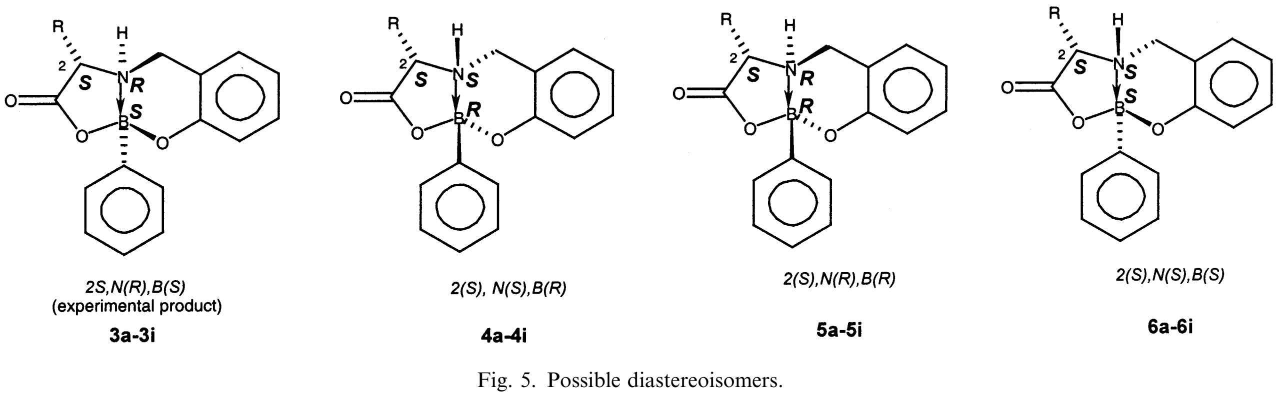
Anal. Found: C, 67.25; H, 5.37; N, 5.32. Calc. for $C_{15}H_{14}BNO_3$: C, 67.45; H, 5.28; N, 5.24%. Suitable crystals were obtained in a 2:1:2 mixture of C_6H_{14}:CH_2Cl_2:CH_3COCH_3.

*4.1.2. (2S,5S,6R)-2-Phenyl-6-aza-1,3-dioxa-5-methyl-2-borabenzocyclononen-4-one (**3b**)*

Compound **3b**. White solid, 83% yield, m.p. (dec.) 211 °C. $[\alpha]_{\mathrm{D}}^{25}=+1.68^{\circ}$ ($c=0.214$, MeOH); IR (ν) (KBr); 3160 (NH), 2924, 1732 (COOB), 1608, 1506 (NH), 1488, 1464, 1330, 1296, 1280, 1236, 1048, 1036, 960, 754, 696 cm^{-1}; MS *m/z* (%): 282 ($M^{+}+1$, 4), 281 (M^{+}, 18), 204 (48), 203 (81), 202 (51), 194 (10), 177 (13), 176 (100), 175 (27), 159 (12), 149 (11), 148 (10), 134 (11), 132 (12), 107 (16). Anal. Found: C, 68.53; H, 5.65; N, 4.94. Calc. for $C_{16}H_{16}BNO_3$: C, 68.36; H, 5.74; N, 4.98%.

*4.1.3. (2S,5S,6R)-2-Phenyl-6-aza-1,3-dioxa-5-iso-propyl-2-borabenzocyclononen-4-one (**3c**)*

Compound **3c**. White solid, 78% yield, m.p. 221–222 °C. $[\alpha]_{\mathrm{D}}^{25}=+2.75^{\circ}$ ($c=0.218$, MeOH); IR (ν) (KBr); 3126, 3072, 2968, 2880, 1724 (COOB), 1720 (COOB), δ 1506 (NH), 1488, 1464, 1330, 1290, 1280, 1232, 1204, 1076, 1040, 974, 758, 704 cm^{-1}; MS *m/z* (%): 310 ($M^{+}+1$, 5), 309 (M^{+}, 21), 233 (10), 232 (76), 231 (37), 205 (17), 204 (100), 203 (25), 189 (11), 188 (14), 187 (10), 148 (15), 134 (29), 107 (19). Anal. Found: C,



2S,N(R),B(S)
(experimental product)
3a-3i

2(S), N(S),B(R)
4a-4i

2(S),N(R),B(R)
5a-5i

2(S),N(S),B(S)
6a-6i

Fig. 5. Possible diastereoisomers.

Table 5
AM1 parameters for compounds **3a**–**3i**, **4a**–**4i**, **5a**–**5i** and **6a**–**6i**

Compound	ΔH_f^o (kcal mol^{-1})	d(N→B) (Å)	θ(O–B–N)$O_{carboxylate}$ (°)	θ(O–B–N)$O_{phenolic}$ (°)	θ(O–B–C)$O_{carboxylate}$ (°)	θ(O–B–C)O_{ph} (°)	θ(N–B–C) (°)	θ(O–B–O) (°)	ϕ(H–N–B–C) (°)	THC (%)
3a	−3826.48	1.688	103.12	113.31	114.29	112.05	108.69	105.13	2.83	74.77
5a	−3811.40	1.701	98.22	103.72	112.35	117.94	112.94	109.60	−170.15	64.57
3b	−4107.38	1.679	103.33	113.61	114.00	111.82	109.06	104.78	4.80	75.27
4b	−4103.25	1.693	103.67	112.17	114.40	116.91	107.35	101.61	8.67	65.72
5b	−4092.69	1.694	98.80	103.23	112.51	117.21	113.36	109.85	168.04	64.56
6b	−4090.89	1.690	98.20	103.49	111.90	116.86	115.07	109.49	−169.40	63.72
3c	−4668.06	1.676	103.18	113.67	114.13	111.64	109.18	104.81	4.31	75.07
4c	−4662.71	1.684	102.69	113.84	115.08	115.20	108.10	101.28	17.61	64.39
5c	−4653.44	1.695	98.86	103.23	112.56	117.04	113.44	109.87	167.22	64.68
6c	−4650.62	1.689	98.41	103.86	112.36	116.89	114.79	108.67	−169.44	63.22
3d	−4950.86	1.677	103.35	113.69	113.96	111.74	109.14	104.72	4.65	75.36
4d	−4946.56	1.688	103.55	112.68	114.53	116.09	107.93	101.38	9.63	66.18
5d	−4934.43	1.691	98.39	103.98	112.45	117.66	113.00	109.38	170.42	65.16
6d	−4931.04	1.686	98.19	103.57	112.09	116.62	115.30	109.24	−169.27	63.32
3e	−4948.65	1.678	103.23	113.56	114.16	111.89	108.97	104.77	7.98	74.84
4e	−4943.79	1.683	102.78	113.52	114.99	115.32	108.13	101.15	16.41	64.70
5e	−4934.35	1.691	98.66	103.41	112.55	117.16	113.39	109.80	168.47	64.63
6e	−4931.64	1.689	98.32	103.84	112.30	116.86	114.95	108.70	−169.81	63.06
3f	−5418.00	1.670	103.20	113.95	113.65	112.26	109.77	103.61	16.07	73.53
4f	−5411.44	1.689	103.15	113.09	114.49	115.90	107.94	101.58	14.23	65.77
5f	−5404.02	1.691	98.91	103.54	112.23	117.12	113.36	109.88	168.61	65.40
6f	−5394.37	1.684	97.99	101.42	111.25	114.10	120.22	110.39	163.33	58.28
3g	−4728.36	1.680	103.32	113.57	113.94	112.31	108.60	104.83	−3.68	74.37
4g	−4725.99	1.688	103.25	113.54	114.64	111.78	108.70	104.71	−0.91	74.11
5g	−4713.81	1.697	98.95	102.96	112.46	117.07	113.65	109.90	−166.91	64.26
6g	−4712.00	1.686	98.40	103.91	111.97	116.88	114.77	109.11	169.70	64.22
3h	−5031.35	1.680	103.38	113.33	114.43	111.81	108.58	105.10	2.44	74.99
4h	−5027.61	1.687	102.87	113.61	114.75	111.74	108.49	105.17	6.89	73.81
5h	−5015.93	1.678	99.45	102.45	112.09	114.25	117.12	110.17	164.30	63.63
6h	−5012.74	1.685	97.98	103.06	111.51	116.04	117.08	109.41	−168.65	62.02
3i	−5314.26	1.670	103.22	113.96	113.62	112.27	109.83	103.54	16.29	73.42
4i	−5306.41	1.694	102.39	113.82	114.71	111.75	108.19	105.77	12.67	73.41
5i	−5300.30	1.690	98.91	103.56	112.22	117.14	113.35	109.86	168.64	65.44
6i	−5290.52	1.685	97.97	101.34	111.15	114.05	120.42	110.47	−163.22	58.02

69.67; H, 6.67; N, 4.59. Calc. for $C_{18}H_{20}BNO_3$: C, 69.93; H, 6.52; N, 4.53%.

4.1.4. (2S,5S,6R)-2-Phenyl-6-aza-1,3-dioxa-5-iso-butyl-2-borabenzocyclononen-4-one (3d)

Compound **3d**. White solid, 97% yield, m.p. 216–218 °C. $[\alpha]_D^{25} = +14.06°$ ($c = 0.32$, MeOH); IR (ν) (KBr); 3125 (NH), 3076, 3050, 2962, 2896, 1716 (COOB), 1610, 1506 (NH), 1490, 1466, 1456, 1364, 1340, 1302, 1280, 1234, 1224, 1204, 1076, 1044, 974, 752, 702 cm^{-1}; MS m/z (%): 324 ($M^+ + 1$, 5), 323 (M^+, 18), 247 (11), 246 (76), 245 (59), 244 (24), 222 (10), 219 (16), 218 (100), 217 (25), 189 (13), 188 (14), 176 (27), 162 (45), 161 (13), 134 (14), 132 (10), 107 (13). Anal. Found: C, 70.87; H, 6.78; N, 4.25. Calc. for $C_{19}H_{22}BNO_3$: C, 70.61; H, 6.86; N, 4.33%.

4.1.5. (2S,5S,6R)-2-Phenyl-6-aza-1,3-dioxa-5-sec-butyl-2-borabenzocyclononen-4-one (3e)

Compound **3e**. White solid, 84% yield, m.p. 221–222 °C. $[\alpha]_D^{25} = +53.33°$ ($c = 0.195$, MeOH); IR (ν) (KBr); 3124 (NH), 3072, 3050, 2968, 2916, 1720 (COOB), 1510 (NH), 1492, 1434, 1358, 1296, 1256, 1232, 1206, 1112, 1078, 1050, 1042, 1034, 756, 702 cm^{-1}; MS m/z (%): 324 ($M^+ + 1$, 6), 323 (M^+, 21), 247 (13), 246 (89), 245 (34), 222 (11), 219 (18), 218 (100), 217 (25), 189 (17), 188 (13), 162 (19), 134 (28), 107 (17) Anal. Found: C, 70.35; H, 6.98; N, 4.40. Calc. for $C_{19}H_{22}BNO_3$: C, 70.61; H, 6.86; N, 4.33%. Suitable crystals were obtained in a 2:1:2 mixture of C_6H_{14}:CH_2Cl_2:CH_3COCH_3.

4.1.6. (2S,5S,6R)-2-Phenyl-6-aza-1,3-dioxa-5-(4′-hidroxybenzyl)-2-borabenzocyclononen-4-one (3f)

Compound **3f**. White solid, 78%, yield m.p. 151–152 °C. $[\alpha]_D^{25} = +2.6°$ ($c = 0.192$, MeOH); IR (ν) (KBr); 3260 (NH), 3074, 3050, 3014, 2928, 1726 (COOB), 1612, 1516 (NH), 1488, 1464, 1450, 1434, 1368, 1350, 1334, 1314, 1300, 1264, 1238, 1110, 1048, 1040, 1028, 976, 960, 890, 846, 764, 742, 702 cm^{-1}; MS m/z (%): 374 ($M^+ + 1$, 4), 373 (M^+, 16), 297 (12), 296 (69), 295 (20), 268 (36), 267 (13), 208 (17), 188 (15), 134 (22), 108 (12), 107 (100). Anal. Found: C, 70.31; H, 5.70; N, 3.83. Calc. for $C_{22}H_{20}BNO_4$: C, 70.80; H, 5.40; N, 3.75%.

4.1.7. (2S,5S,6R)-2-Phenyl-6-aza-1,3-dioxa-5-(2-methylsulfanyl-ethyl)-2-borabenzocyclononen-4-one (3g)

Compound **3g**. White solid, 76% yield, m.p. (dec.) 230 °C $[\alpha]_D^{25} + 2.57°$ ($c = 0.201$, MeOH); IR (ν) (KBr); 3124 (NH), 3072, 3048, 3012, 2918, 2850, 1740 (COOB), 1734 (COOB), 1718, 1702, 1516 (NH), 1488, 1464, 1434, 1340, 1280, 1236, 1206, 1112, 1078, 1042, 976, 760, 708 cm^{-1}; MS m/z (%): 342 ($M^+ + 1$, 6), 341 (M^+, 28), 265 (15), 264 (91), 263 (31), 237 (15), 236 (100), 235 (27), 209 (14), 208 (53), 207 (13), 202 (10), 190 (14), 189 (10), 188 (55), 187 (26), 174 (17), 162 (17), 148 (10), 107 (21), 61 (52), 56 (15). Anal. Found. C, 63.95; H, 5.80; N, 4.02; S, 9.40. Calc. for $C_{18}H_{20}BNO_3S$: C, 63.36; H, 5.91; N, 4.10; S, 9.40%.

4.1.8. 2,5-Diphenyl-6-aza-1,3-dioxa-2-borabenzocyclononen-4-one (3h)

Compound **3h**. White solid, 68% yield, m.p. 213–215 °C. IR (ν) (KBr); 3102 (NH), 3072, 2896, 1744 (COOB), 1724 (COOB), 1512 (NH), 1490, 1464, 1446, 1372, 1352, 1326, 1290, 1264, 1244, 1076, 1042, 1010, 978, 950, 764, 756, 744, 702 cm^{-1}; MS m/z (%): 344 ($M^+ + 1$, 5), 343 (M^+, 19), 299 (15), 266 (42), 265 (26), 264 (11), 239 (27), 238 (100), 237 (27), 222 (13), 221 (20), 211 (24), 210 (12), 194 (29), 193 (14), 148 (38), 107 (16), 106 (15), 104 (10), 90 (10). Anal. Found. C, 73.95; H, 5.47; N, 4.25. Calc. for $C_{21}H_{18}BNO_3$: C, 73.50; H, 5.29; N, 4.08%. Suitable crystals were obtained in a 2:1:2 mixture of C_6H_{14}:CH_2Cl_2:CH_3COCH_3. The existence of a racemic mixture was established by ^1H and ^{13}C-NMR experiments using Europium tris(3-(heptafluoropropyl-hydroxymethylene)-(-)-camphorate [44].

4.1.9. (2S,5S,6R)-2-Phenyl-6-aza-1,3-dioxa-5-benzyl-2-borabenzocyclononen-4-one (3i)

Compound **3i**. White solid, 74% yield, m.p. 183–185 °C. $[\alpha]_D^{25} = -27.01°$ ($c = 0.213$, MeOH); IR (ν) (KBr); 3258 (NH), 3126, 2920, 1732 (COOB), 1608, 1506 (NH), 1488, 1464, 1330, 1296, 1280, 1236, 1048, 1036, 960, 754, 696 cm^{-1}; MS m/z (%): 358 ($M^+ + 1$, 5), 357 (M^+, 18), 281 (18), 280 (100), 279 (36), 253 (17), 252 (84), 251 (21), 188 (24), 148 (10), 134 (29), 107 (29), 91 (40). Anal. Found. C, 74.35; H, 5.60; N, 3.70. Calc. for $C_{22}H_{20}BNO_3$: C, 73.97; H, 5.64; N, 3.92%.

4.2. X-ray structures of boronates 3a, 3e and 3h

Crystallographic data for **3a**, **3e** and **3h** were acquired on an Enraf Nonius-CAD4 diffractometer, using Mo–K_α radiation with graphite monochromator at 293 K and the $\omega - 2\theta$ scan mode technique for both unit-cell determination and data collection. Crystals were mounted in LINDEMAN tubes. All data were corrected for Lorentz and polarization effects. Absorption correction was performed with SHELX-A procedure [45]. The structures were solved using direct methods with the SHELX-S-97 and SHELX-L-97 ver. 34 programs for refinement and data output [45], included in WIN-GX program set [46]. The corresponding images were prepared with ORTEP 3 program [47]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and one overall isotropic thermal parameter was refined.

5. Supplementary material

Tables of crystallographic parameters, atomic coordinates, anisotropic thermal parameters, bond distances, bond angles as well as a list of the structural factors have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 172020 for **3a**, 172021 for **3e**, 172022 for **3h**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support and scholarships to H.I.B. and L.S.Z. from the Consejo Nacional de Ciencia y Teconología (CONACyT, México) is acknowledged. The authors would like to thank QFI Dolores Castillo for the IR spectra, Q.I. Victor Gonzalez for NMR spectra and to IMP (Instituto Mexicano del Petróleo) for elemental analyses determinations.

References

[1] G.H.L. Nefkens, B. Zwanenburg, Tetrahedron 41 (1985) 6063.
[2] J.H. Ritsma, Rec. Trav. Chim. Pays-Bas 94 (1975) 174.
[3] (a) L.L. Koh, J.O. Ranford, W.T. Robinson, J.O. Svensson, A.L.Ch. Tan, D. Wu, Inorg. Chem. 35 (1996) 6466;
(b) J.D. Ranford, J.J. Vittal, D. Wu, Angew. Chem. Int. Ed. Engl. 37 (1998) 1114.
[4] (a) C.A. Suresham, R.K. Bhattacharya, J. Chem. Res. (S) (1998) 552(b) C.A. Suresham, R.K. Bhattacharya, J. Chem. Res. (M) (1998) 2186.
[5] M.S. Shongwe, M. Mikuriya, R. Nukada, E.W. Ainscough, A.M. Brodie, J.M. Waters, Inorg. Chim. Acta 290 (1999) 228.
[6] (a) J.G. Wilson, Aust. J. Chem. 43 (1990) 1283;
(b) J.G. Wilson, Aust. J. Chem. 41 (1988) 173;
(c) J.G. Wilson, Aust. J. Chem. 43 (1990) 783.
[7] H. Höpfl, N. Farfán, J. Organomet. Chem. 547 (1997) 71.
[8] H. Höpfl, M. Sánchez, N. Farfán, S. Rojas, R. Santillan, Inorg. Chem. 37 (1998) 1679.
[9] V. Barba, D. Cuahutle, M.E. Ochoa, R. Santillan, N. Farfán, Inorg. Chim. Acta 303 (2000) 7.
[10] N. Farfán, H. Höpfl, V. Barba, M.E. Ochoa, R. Santillan, E. Gómez, A. Gutierrez, J. Organomet. Chem 581 (1999) 70.
[11] V. Barba, R. Luna, D. Castillo, R. Santillan, N. Farfán, J. Organomet. Chem. 604 (2000) 273.
[12] N. Farfán, R. Santillan, H. Höpfl, Main Group Chem. News 7 (1999) 3.
[13] V. Barba, E. Gallegos, R. Santillan, N. Farfán, J. Organomet. Chem. 622 (2001) 259.
[14] R. Contreras, C. García, T. Mancilla, J. Organomet. Chem. 246 (1983) 213.
[15] T. Mancilla, R. Contreras, B. Wrackmeyer, J. Organomet. Chem. 307 (1986) 1.
[16] T. Mancilla, R. Contreras, J. Organomet. Chem. 321 (1987) 191.
[17] N. Farfán, T. Mancilla, D. Castillo, G. Uribe, L. Carrillo, P. Joseph-Nathan, R. Contreras, J. Organomet Chem. 381 (1990) 381.
[18] V. Barba, D. Cuahutle, R. Santillan, N. Farfán, Can. J. Chem. 79 (2001) 1229.
[19] E.B. Fleischer, R. Dewar, Tetrahedron Lett. (1970) 363.
[20] W. Kliegel, S.J. Rettig, J. Trotter, Can. J. Chem. 62 (1984) 515.
[21] W. Kliegel, D. Nanninga, S.J. Rettig, J. Trotter, Can. J. Chem. 62 (1984) 845.
[22] S.M.S.V. Doidge-Harrison, O.C. Musgrave, J.L. Wardell, J. Chem. Crystallogr. 28 (1998) 361.
[23] N. Farfán, P. Joseph-Nathan, L.M. Chiquete, R. Contreras, J. Organomet. Chem. 348 (1988) 149.
[24] W. Kliegel, G. Lubkowitz, S.J. Rettig, J. Trotter, Can. J. Chem. 71 (1993) 2129.
[25] P.D. Woodgate, G.M. Hornel, N.P. Maynard, C.E.F. Rickard, J. Organomet. Chem. 592 (2000) 188.
[26] P.D. Woodgate, G.M. Hornel, N.P. Maynard, C.E.F. Rickard, J. Organomet. Chem. 595 (2000) 215.
[27] T. Mancilla, H. Höpfl, G. Bravo, L. Carrillo, Main Group Met. Chem. 20 (1997) 31.
[28] S.J. Rettig, J. Trotter, Can. J. Chem. 53 (1975) 1393.
[29] S. Caron, J.M. Hawkins, J. Org. Chem. 63 (1998) 2054.
[30] R.A. Howie, O.C. Musgrave, J.L. Wardell, Main Group Met. Chem. 20 (1997) 723.
[31] H. Arnt, W. Kliegel, S.J. Rettig, J. Trotter, Can. J. Chem. 68 (1990) 1791.
[32] S.J. Rettig, J. Trotter, W. Kliegel, H. Becker, Can. J. Chem. 54 (1976) 3142.
[33] W. Kliegel, G. Lubkowitz, S.J. Rettig, J. Trotter, Can. J. Chem. 70 (1992) 2015.
[34] W. Kliegel, G. Lubkowitz, S.J. Rettig, J. Trotter, Can. J. Chem. 70 (1992) 2027.
[35] W. Kliegel, G. Lubkowitz, S.J. Rettig, J. Trotter, Can. J. Chem. 70 (1992) 2809.
[36] H.I. Beltrán, A. Abreu, L.S. Zamudio-Rivera, T. Mancilla, R. Santillan, N. Farfán, Rev. Soc. Quim Mex. 45 (2001) 152.
[37] A. Haaland, Angew. Chem. Int. Ed. Engl. 28 (1989) 992.
[38] H. Nöth, B. Wrackmeyer, Nuclear magnetic resonance spectroscopy of boron compounds, Springer-Verlag, Berlin, New York, 1978, p. 461.
[39] L. Stefaniak, G.A. Webb, M. Witanowski, Annu. Rep. NMR Spectrosc. 18 (1986) 72.
[40] N. Farfán, D. Silva, R. Santillan, Heteroat. Chem. 4 (1993) 553.
[41] J. Trujillo, H. Höpfl, D. Castillo, R. Santillan, N. Farfán, J. Organomet. Chem. 571 (1998) 21.
[42] H. Höpfl, J. Organomet. Chem. 581 (1999) 129.
[43] HyperChem v.5, Hypercube Inc. 115 NW 4th Street, Gainesville, FL, USA.
[44] D. Parker, Chem. Rev. 91 (1991) 1441.
[45] G. M. Sheldrick, SHELX-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1993.
[46] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837 (Win GX program Set).
[47] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 837 (ORTEP 3).